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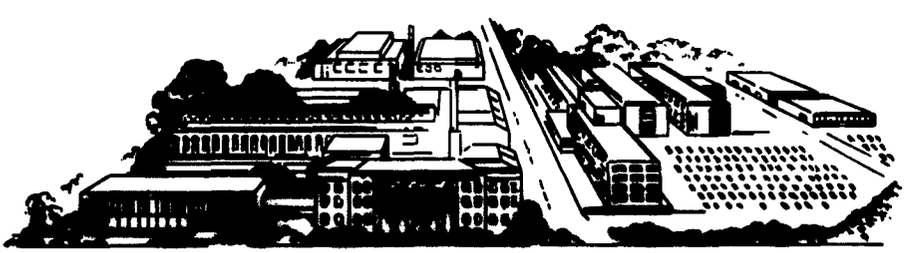

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SECOND QUARTERLY REPORT

on

MECHANISM OF WATER ABSORPTION IN GLASS-REINFORCED PLASTICS

to

DEPARTMENT OF THE NAVY
BUREAU OF SHIPS

January 1, 1963

by

D. W. McNeil, B. Bennett, and R. I. Leininger

Contract No. NObs 86871
Project No. SR-007-03-04
Task No. 1008
BuShips No. 98-1008-10

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February 1, 1963

Department of the Navy
Bureau of Ships
Washington 25, D. C.

Attention Code 634 C.

Gentlemen:

Enclosed is the Second Quarterly report on your project "Mechanism of Water Absorption in Glass-Reinforced Plastics", Contract No. NObs 86871. This report covers activities from October 1, 1962, to January 1, 1963.

Included are a description of an optical method for following diffusion phenomena in cured-resin systems and the results from several long-term immersion studies. Several model systems representing conditions peculiar to glass-reinforced plastics are being utilized for clarification of possible mechanisms of moisture penetration.

Any questions or comments pertinent to this work will be welcomed.

Very truly yours,

D. W. McNeil
Polymer Research

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MECHANISM OF WATER ABSORPTION IN GLASS-REINFORCED PLASTICS

by

D. W. McNeil, B. Bennett, and R. I. Leininger

INTRODUCTION

As one phase of the Navy's deep-submergence program, this study is designed to clarify the phenomena occurring during immersion of glass-reinforced epoxide resins in aqueous media. It is known that moisture is absorbed, with a resultant deterioration in mechanical properties. Therefore, knowledge gained as to mode of entry and destination of the absorbed moisture should provide a basis for the design and application of remedial measures.

This report covers work completed between October 1, 1962, and January 1, 1963.

SUMMARY

During the second quarter, work was evenly divided between the two phases of this program. The first of these, the resin study, consisted primarily of the design, construction, and utilization of an optical diffusimeter suitable for the quantitative investigation of pressure effects upon moisture-absorption rates in typical epoxy resins. Based upon the principle of light refraction, this instrument is capable of providing an accurate photographic record of the state of diffusion in the polymer at any given time. From this record, distance diffused and localized concentration variations can be calculated. Tentative evidence of moisture diffusion into an anhydride-cured resin has already been obtained, although time has permitted the performance of only two experiments with this equipment. Quantitative interpretation of future experiments will be attempted on the basis of this work.

Immersion studies of both filament-wound and cast-resin test cylinders have been continued from the preceding quarter. It has been observed that moisture absorption is more predictable among the resin cylinders than among the filament-wound group. Upon removing these cylinders from the pressure chamber after 10 weeks of immersion, cracks were observed in the inner walls of approximately 50 per cent of the resin cylinders. Some of these cracks were quite severe. Hence, it may be necessary to modify this phase of the resin study.

Moisture absorption in filament-wound test cylinders appears to be a more random phenomenon. Disregarding those samples in which leakage had obviously occurred at the end caps, considerable variance is still observed between apparently identical specimens. The numerous theories as to the reason for this data spread are being tested by the use of several "model systems" to simulate conditions peculiar to typical laminate structures. Light microscopy is also being utilized, both in the evaluation of these model

systems and in the evaluation of quality of experimental laminates and immersion damage. To date, no evidence of the latter has been observed by microscopic methods.

Once the concentration-distance-time relationship has been established for the epoxy resin - water system, the curves presented in the Appendix of this report will be re-evaluated. Diffusion measurements upon glass-reinforced resin films containing a minimum number of fibers will also be made to determine whether anisotropic diffusion phenomena are possible in such systems.

EXPERIMENTAL WORK*

Diffusion Measurements

Initial experiments have suggested moisture absorption in glass-reinforced epoxy laminates to be a relatively slow process when a minimum number of fibers are exposed to the immersion medium. Immersion studies upon filament-wound test cylinders have demonstrated considerable variation in moisture pickup from sample to sample, while similar data obtained from cast resin cylinders were more constant. From these observations, it may be tentatively inferred that moisture may "enter" the laminate either by the relatively slow process of diffusion or by more rapid conduction along any flaw which may originate at or near the surface of the test vessel. The latter phenomenon will become evident by a random data spread within a group of similar specimens, while diffusion phenomena have been shown[1-10]** to exhibit well-defined behavior patterns which may be readily reduced to mathematical expressions describing the behavior of given systems and conditions.

Numerous investigators[11-18] have described diffusion phenomena in polymer systems. However, the bulk of this work appears to have been directed toward polymer-solvent systems[17, 18] and polymer-gas systems[11, 14, 15, 16]. Very few data have been reported for polymer-nonsolvent systems, especially in the case of a rigid, highly crosslinked structure such as a cured epoxide-based resin.

Several methods have been employed in the study of diffusivity. Many of these require complex mathematical treatments as well as elaborate equipment unsuitable for the investigation of high-pressure effects. In techniques such as layer analysis, it is necessary to make various assumptions which preclude the realization of accurate results. Various optical techniques, however, have been successfully employed for the determination of diffusivity in transparent systems. Typical of these are Schlieren and interferometric devices. Based upon the principle of light refraction, these instruments are capable of giving quantitative data from which both diffusion coefficients and concentration distributions can be obtained.

The initial literature search disclosed several devices which might possibly be utilized in the investigation of diffusion phenomena at elevated pressures. The method selected was essentially a modification of Robinson's technique for measuring the penetration of cellulose acetate by chloroform and other solvents[17, 18, 19]. It was felt

* Original data are found in Battelle Notebooks Nos. 19390 and 19610.

** See section on References, page 16.

that this technique was the only one possessing sufficient sensitivity for detection of the relatively small refractive index changes accompanying the diffusion of water into cured epoxy resin systems, yet still lending itself to modification for the investigation of pressure effects. No commercially available instruments were found to be adaptable to this technique. Hence, it was necessary to design and construct special apparatus.

Equipment

The diffusimeter consists of three basic parts: an illumination system, a pressure cell containing the sample within the interferometer, and a viewing system. In Figure 1, the illuminating system is to the right of the pressure cell and the viewing system to the left.

The light source is a G. E. Type H-4 mercury-vapor lamp. A filter transmits only the green wavelength which is projected by the condenser upon a diaphragm adjustable in a plane normal to the optic axis of the instrument. A 5X microscope objective serves as a collimator.

The pressure cell itself was turned from a Monel forging (see Figure 2). Other materials could have been used. However, it is planned to investigate electrolyte effects using a salt-water immersion medium. Metals such as stainless steel therefore become unsuitable due to the possibilities of stress corrosion. The windows are made from fused quartz and are flat to within 1/4 wavelength of sodium light. They are held in place by retaining rings backed up by heavy threaded nuts. Neoprene O-ring seals prevent leakage. Samples are inserted by removing one of the windows.

The viewing system presented several difficulties during construction of the diffusimeter. It was not feasible to use a conventional microscope body since the maximum working (objective to specimen) distance is in most cases at best only 15-20 mm. The sample is located 3 inches inside the pressure cell, and the 3/4-inch-thick quartz windows refract the light in such a manner as to add another 1/16-1/8 inch to the total minimum working distance required. This problem was solved by obtaining a lens-type erecting assembly (5X magnification) from a surplus riflescope and geometrically computing the point at which a standard 10X Huygenian microscope eyepiece should be placed to provide additional magnification. Although some of the peripheral rays from the "objective (the riflescope erecting assembly) are masked by the small aperture of the eyepiece, the light source is sufficiently intense that the sample image may be viewed on the ground glass of the camera without having to extinguish the room lights. This system has been tested and found to be reasonably free from the more serious lens aberrations. Magnifications from 50 to 100X may be obtained by varying the distance of the film plane from the microscope eyepiece.

The pressure source (Figure 3) consists of a standard (commercially available*) "dead weight tester". The pressure produced in the master cylinder (not visible in the figure) is balanced against a piston in a second cylinder. This piston is connected through a linkage to the scales in such a manner that it requires 1,000 psi to balance 1 pound of weight. The pressure can be accurately controlled within 1/2 per cent. Since the unit uses oil as the pressure medium, a mercury seal is utilized to separate oil from the water-immersion medium.

* Crosby Steam Gauge & Valve Company.

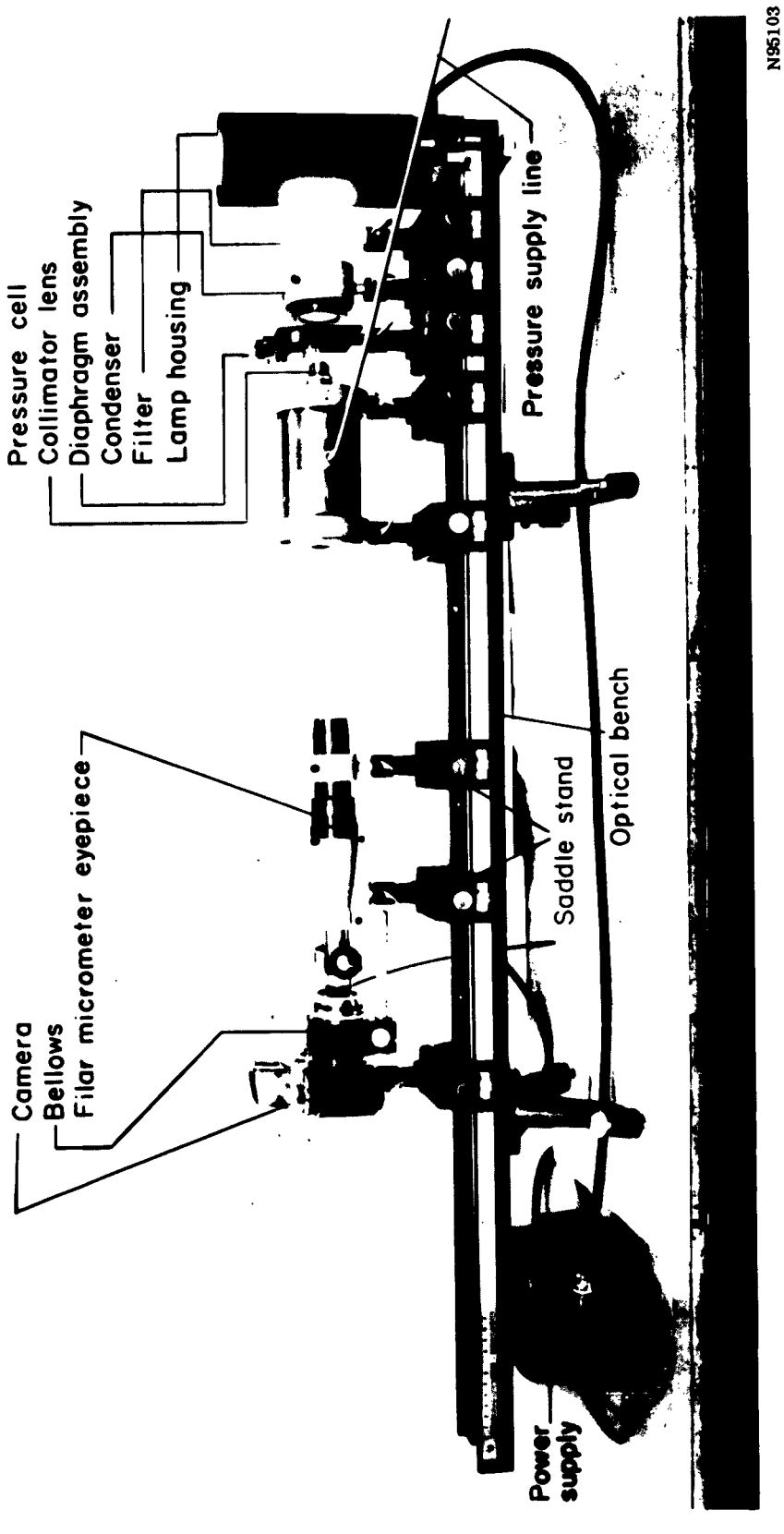

FIGURE 1. OPTICAL DIFFUSIMETER

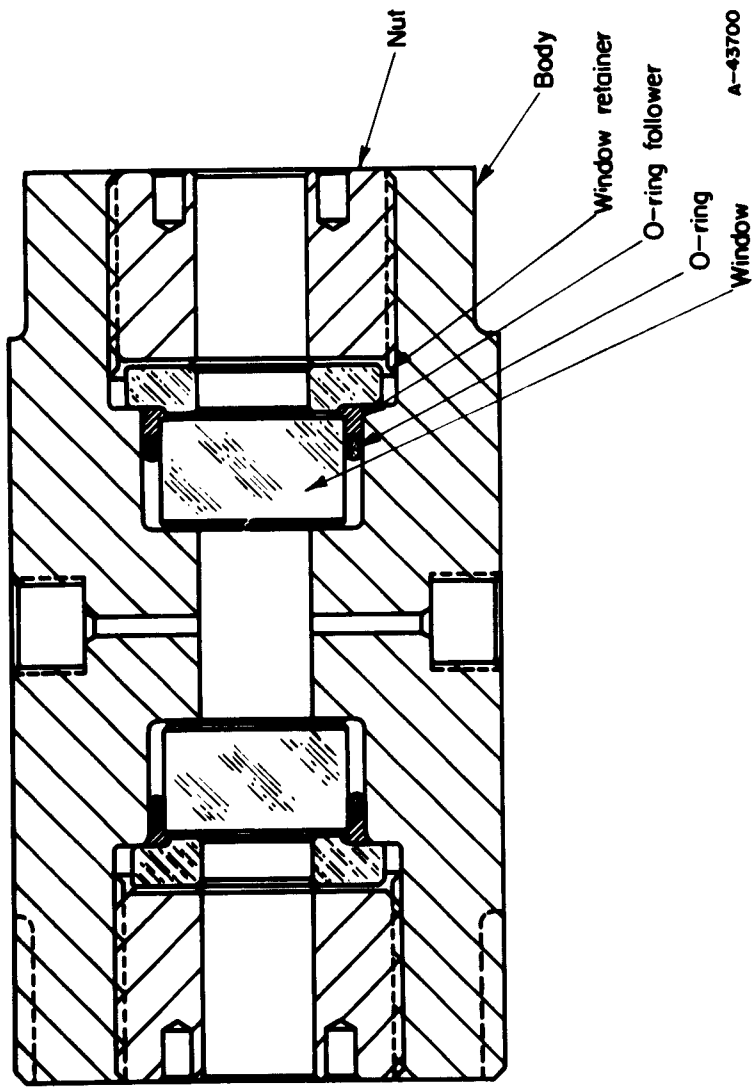

FIGURE 2. DIAGRAM OF HIGH-PRESSURE CELL

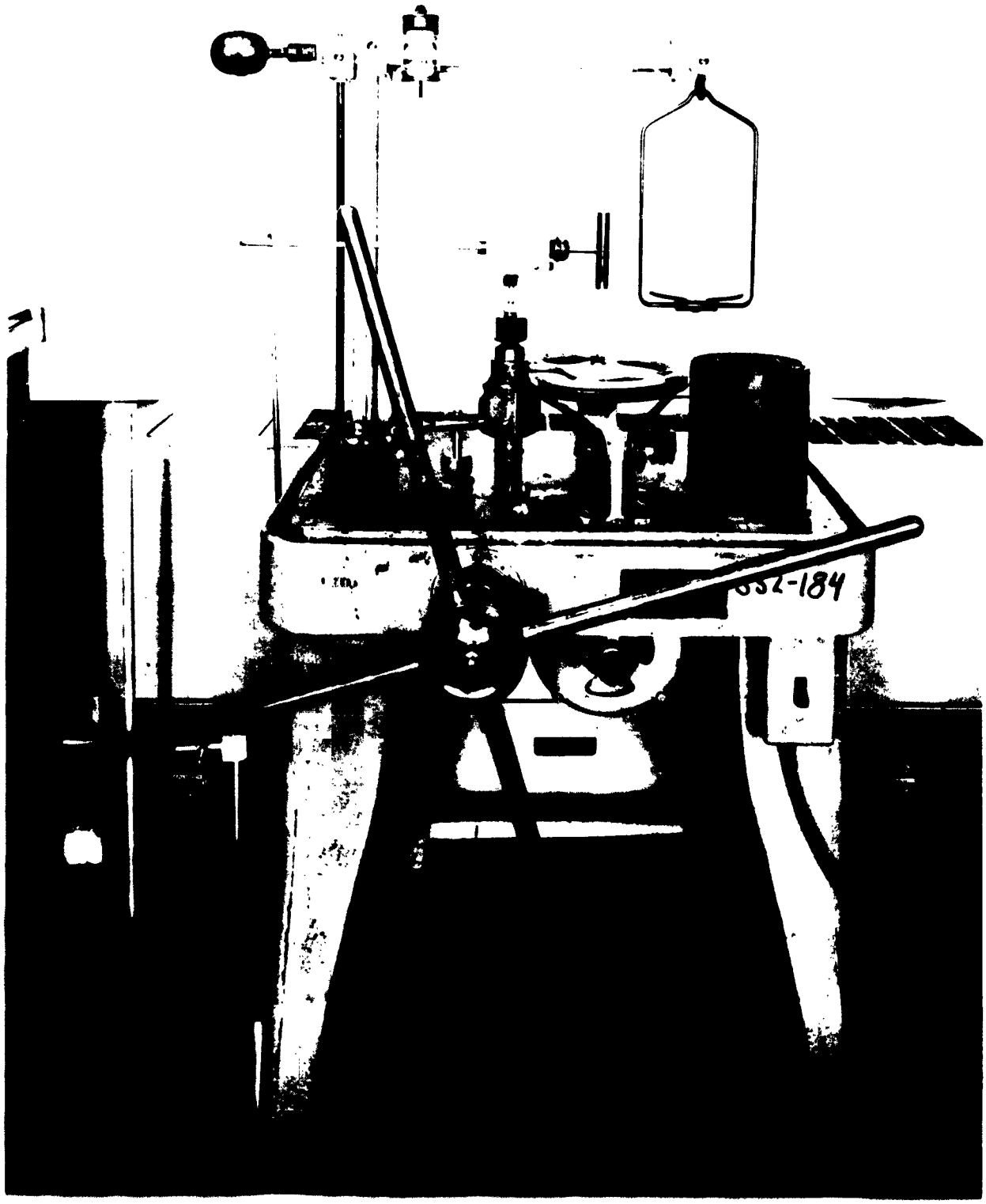

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FIGURE 3. PRESSURE SOURCE FOR DIFFUSIMETER

Principle of Operation (Theory)

When a beam of light passes from one transparent medium into another at an angle to the interface, it will be bent (refracted) by an amount proportional to the difference in refractive indices of the two media (Snells law of refraction). More specifically

$$\eta = \frac{\sin i}{\sin r}, \tag{1}$$

where i is the angle of incidence and r the angle of refraction. The quantity η is called the relative index of refraction and is a constant for a given system under given conditions. It is customarily determined for an unknown medium with respect to air (relative refractive index) or a vacuum (absolute refractive index). Since the room-temperature refractive indices of a typical cured epoxy resin (~1.5) and of water (~1.3) are different, it is possible to measure this angular displacement. Assuming that the water slowly diffuses into the cured resin, the initially measured angular displacement and hence the refractive index of the resin will change. In effect, a third (optical) medium has been interposed in the system. These refractive index changes are directly relatable to concentrations, and by selection of the appropriate method it becomes possible to accurately measure the quantity of water which the polymer may absorb and hold in any given interval. (In practice, it is convenient to consider angular displacement merely as implied by the refractive index.)

Perhaps the most sensitive methods for measuring these slight refractive index changes are those based upon interferometry. The term, "interferometer", is perhaps best defined by Jonnard[20]:

> "It is an instrument capable of splitting a monochromatic sinusoidal wave train of given frequency into two or more coherent beams and allowing these beams to become superimposed again after a variable path, in such a way that the resulting instantaneous sum sine wave amplitude can be detected".

The detection is usually accomplished by observing the shift in position and spacing of a series of interference fringes appearing across the field of view.

The interferometer selected for use in the subject study is the multiple-beam type. It consists of two partially aluminized optically flat glass plates arranged parallel to each other with the silvered surfaces in contact with the sample which is cured in situ. The wedge angle between these surfaces is adjusted to ~0°. Upon viewing the resin-water interface, a series of alternately light and dark bands is observed to cross the field. As light passes through this device, multiple reflections occur between the aluminized surfaces. Assuming light to be a sinusoidal electromagnetic vibration, it may be shown[20] that bright fringes are the result of coincidence of the maxima of the multiple beams, while the dark fringes are the result of coincidence of the minima. The path taken by these beams is expressed as the optical path:

$$\text{Optical path} = \sum_i \eta_i \, d_i, \tag{2a}$$

where η is the refractive index of the medium and d the distance traveled between reflections. In a single medium, this becomes:

$$\text{Optical path} = \eta d. \tag{2b}$$

If, therefore, in a single field there is visible a region of known refractive index (e.g., water), the refractive index change at any other point can be obtained by applying Robinson's equation:

$$\Delta\mu = \frac{\lambda}{2\bar{T}}\left(1 \pm \frac{\bar{\mu}\Delta x}{f\mu_L}\cos\phi\right), \tag{3}$$

where

$\Delta\mu$ = change in refractive index
λ = wavelength of light
$\bar{T}$ = mean sample thickness
$\bar{\mu}$ = mean refractive index in changing area
Δx = distance diffused
f = fringe spacing
μ_L = refractive index of water
ϕ = the angle between a linear fringe in the water and the outer boundary of the zone of diffusion.

The sign of the last expression in parentheses is dependent upon whether diffusion is toward the apex of the wedge$^{(-)}$, or away from the apex$^{(+)}$.

Normally, this equation may be considerably simplified for certain specialized cases such as where the wedge angle formed by the interferometer plates is 0° or diffusion is parallel to the fringes. The equation becomes:

$$\Delta\mu = \frac{\Delta\mu_N}{N},$$

where

$\Delta\mu_N$ = known refractive index difference between two points
N = number of fringes between these two points.

In the work with epoxy resin - water systems, the interferometers are prepared in such a manner as to satisfy this latter equation.

Preparation of Samples for Interferometry

The interferometer plates for these experiments are 1/2-inch-diameter by 1/4-inch-thick optically flat (1/4 wave) glass plates upon which a 90 per cent reflecting aluminum film has been deposited by evaporation in vacuum. A minute droplet of epoxy resin is placed in the center of one of the plates, and spacers are placed around the periphery. The second plate is then pressed onto this assembly and clamped in such a

manner that a well-spaced fringe system is viewed with monochromatic light. The device is then heat cured and allowed to cool slowly over a period of about 16 hours. A complete interferometer is shown in Figure 4.

a. Individual Flats Before Assembly

b. Assembled Interferometer Spacers Not Shown

FIGURE 4. INTERFEROMETER

Initially, it was found that the aluminum film acted as a relatively good parting agent and the assembly could be broken, leaving the aluminum film attached to the resin droplet. Instead of using a mercury vacuum system (at pressures of 1×10^{-5} mm of Hg), all subsequent aluminizing was conducted at pressures of 5×10^{-9} using a titanium vapor ion pump. Interferometers prepared from plates so coated were structurally quite strong, and no clamping mechanism was found necessary after cure of the resin.

A second problem arose when the first immersion studies were conducted. The aluminum film in contact with the water was observed to completely disappear (possibly due to electrolytic action) after about 25 hours' immersion, with the result that the water fringe pattern was no longer visible. Hence, any change in wedge angle could not be detected. This difficulty was solved by overcoating all flats with a layer of silicon monoxide. Several assemblies so prepared have been observed to suffer no loss in reflectivity after 300 hours' immersion.

Diffusion Runs

Two initial immersion studies at normal pressures have been conducted, the longer of which lasted 46 hours. At the end of this time, the experiment was terminated since the solvent fringes could no longer be observed. Hence, any further change in wedge angle could not be followed. Four interferograms taken at various time intervals during this experiment are shown in Figure 5. Figure 5a shows the initial fringe pattern before water has been added to the cell. The paddle shaped outline is the edge of a polymer film between the interferometer plates. In 5b, the edge of the film has been in contact with the water for 2 hours. Note the appearance of a new fringe at the resin-water interface. After 23 hours this fringe has become well defined and moved farther into the resin. Figures 5c and 5d show the condition of the polymer film after 23 and 46 hours' immersion, respectively. The experiment was terminated at this point since the water fringes could no longer be observed.

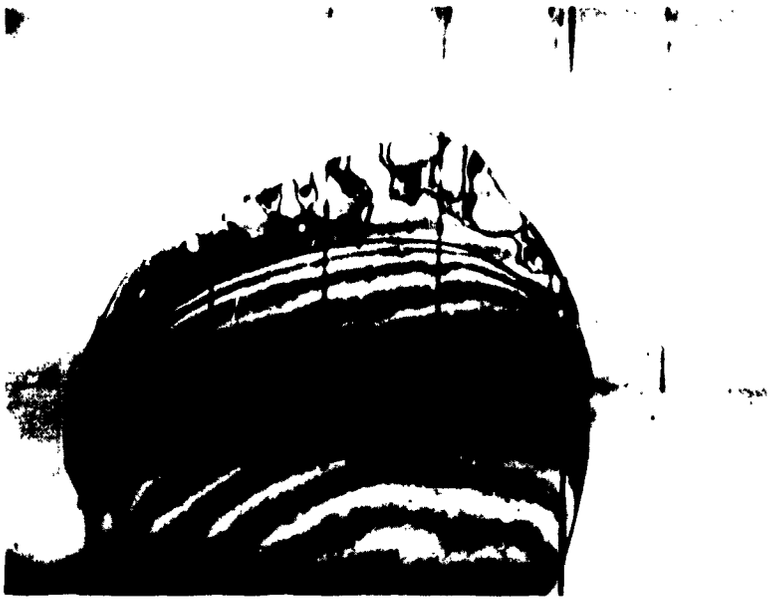
a. Initial Fringe Pattern Before Addition of Water

Resin outline

b. Fringe Pattern After 2-Hr Immersion

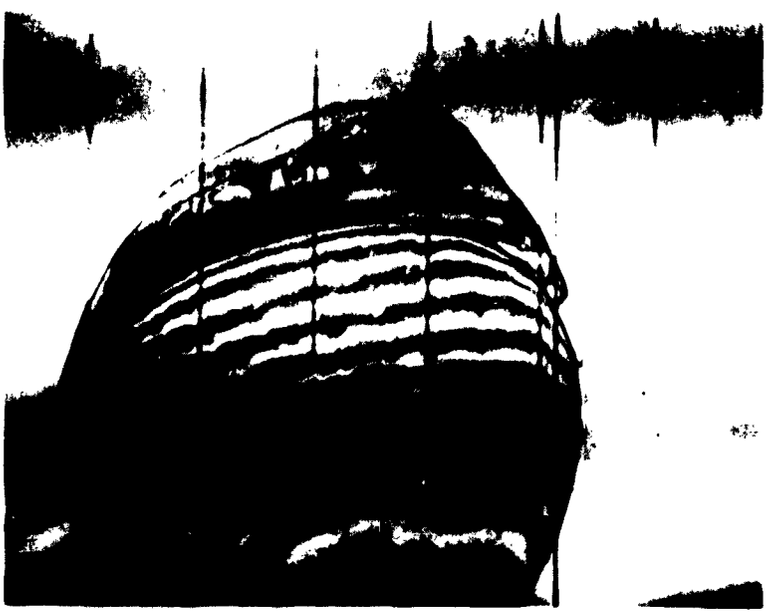
Note the appearance of eleventh fringe.

FIGURE 5. INTERFEROGRAMS TAKEN DURING IMMERSION OF A 1-MIL CURED-EPOXY-RESIN FILM AT AMBIENT PRESSURE



c. Eleventh Fringe Well Defined After 23-Hr Immersion

Water fringes disappearing.



d. Eleventh Fringe Well Defined After 46-Hr Immersion

A twelfth fringe is almost apparent (arrow).

FIGURE 5. (CONTINUED)

From these photographs only the most rudimentary analysis can be made, since the experiment had not proceeded to the point where measurements could include a larger number of fringes, as opposed to one as in this instance. However, the following observations can be made:

(1) In the initial interferogram, 10 fringes are visible over the resin field.

(2) After 24 hours, 11 fringes are visible and the width of the fringes at the interface has narrowed slightly.

This behavior gives rise to the tentative conclusion that diffusion of water into a cured epoxy is possible, although relatively slow. Indeed, this is about the only explanation for the appearance of the eleventh fringe, as the temperature was held constant during the experiment and the fringe spacing in the center of the polymer field has not changed. If moisture had penetrated between the aluminum and the resin or between the glass and aluminum, it would be expected that the reflectivity of the aluminum would have also changed in the region where the new fringe appears (as did the water fringes). (The flats used in this experiment were not SiO overcoated.)

A quantitative evaluation of these interferograms was not attempted due to the change in reflectivity in the aluminum in the water field, the presence of a large air bubble, and the appearance of only one new fringe.

In the coming quarter, it is planned to investigate more thoroughly diffusion phenomena in cured epoxy resin systems using a more sensitive interferometer (e. g., a thicker polymer film). Pressure effects will be investigated in a model system (crosslinked gelatin) in order to compress the time interval involved and will furnish the basis for investigating pressure effects in epoxy-resin systems. Both distilled water and saline media will be used in these experiments in order to isolate any effects due to the presence of electrolytes.

Immersion Studies

Two types of sample are being subjected to prolonged immersion at hydrostatic pressures of 10,000 psi. These are filament-wound test cylinders and cast epoxy-resin test cylinders. It has been observed that moisutre absorption in the latter group is more constant and hence more predictable than in the former.

These cast resin test cylinders were prepared from silicone-rubber molds of machined and polished stainless steel master parts. After 1600 hours' immersion at 10,000 psi, moisture pickup by the specimen had been surprisingly constant among similar samples. When the pressure vessel was opened, however, at the end of the tenth week of immersion it was noted that roughly 45 per cent of the resin cylinders had started to crack at the inner surface of the walls. These cracks were not visible 168 hours earlier. Since these cylinders obviously will not survive the elevated pressure much longer, it will be necessary to modify this phase of the resin study. Nevertheless, 1600 hours of weight-gain measurements are available for typical epoxy resin cylinders.

It will be noted from Figures A-1 and A-2 (1-inch and 3/4-inch resin cylinders exposed to 10,000 psi) and Figures A-3 and A-4 (1-inch and 3/4-inch resin cylinders exposed to water at ambient conditions) that there is apparently no difference in the diffusion rates which would be attributed to pressure. In both instances the slope of the curves is roughly the same, indicating similar absorption rates. Slight differences in the displacement of the curves may be attributable to experimental error, since the points are located to the nearest 0.1 mg. It will also be noted that these curves apparently satisfy the Bolzman relationship for free diffusion:

$$C = \int\left(\frac{x}{t1/2}\right),$$

where

c = concentration
x = distance diffused
t = time.

No explanation has yet been found for the inflection occurring at about 600 to 800 hours, both in pressure specimens and in controls. (This same inflection occurs in all cases where the individual values are plotted separately, as well as in plots of average values obtained from like samples - Figures A-1 through A-9.) It could perhaps be due to the start of another phenomena in addition to diffusion.

The capped filament-wound cylinders all had an outer resin layer roughly 1/32-1/16-inch thick formed during fabrication. One-half-inch resin end plates were cemented to each end. In no instance was the cut surface of the filament-wound portion exposed to the immersion medium. From the shape of the resulting curves (Figures A-4 and A-5) it would be logical to assume that the same phenomena are occurring in these samples as in the resin cylinders. Since the actual distance-time diffusion relationship has yet to be established, it is not known whether moisture has penetrated to the underlying glass layers. These data will be reconsidered in future reports once the concentration-distance-time relationship has been established. It should be noted that none of the curves presented in the Appendix show signs of a plateau indicating the formation of equilibrium conditions with the immersion medium.

Once the concentration-distance-time relationship has been established, it is planned to construct several model systems in which a minimum number of fibers have been introduced into the resin film. Using the diffusimeter previously described, measurements will be attempted to ascertain whether strains introduced during cure of the resin produce anisotropy in diffusion rates.

Behavior of the open filament-wound test cylinders proved to be somewhat more erratic in that there was more of a data spread among samples (see Figures A-7, A-8, and A-9). This may conceivably be due to a number of factors. Chief among these are:

(1) Number of flaws originating at the surfaces of the test vessel

(2) Thickness of outer and inner resin layers

(3) Proximity of existing air bubbles to surfaces of vessel

(4) Fiber packing

(5) Resin cracking between fibers due to shrinkage during cure

(6) Number of fibers penetrating surfaces of vessel

(7) Winding pattern.

These theories are being tested both through utilization of light microscopy and by the construction of various model systems.

The first four of the above concepts are readily measured by the preparation of suitably polished embedded specimens, with observation under high magnification using incident illumination. It has been found convenient in this laboratory to measure void content quantitatively by means of the integrating microscope stage.

This device consists of a number of micrometer spindles (usually six) which move the object along the Y-axis of the microscope stage. A single pinion assembly controls the X-axis. As the name of the device would suggest, the specimen is optically divided into line segments. The ratio of the total lengths of line segments falling within any single phase of a heterogeneous substance is directly proportional to the volume of that phase. During measurement, a different spindle is assigned to each component. At the end of each traverse (of predetermined length), the totals from each spindle are recorded. Usually, ten traverses are sufficient to furnish accurate basis for computation. Using this method, a relatively constant 7.6 per cent by volume of trapped air was observed in representative specimens of filament-wound laminates belonging to one lot. Typical fields from such specimens are shown in Figure 6. The volumetric analysis for the specimen on which these fields were observed is shown in Table A-1 of the Appendix.

It has been suggested by Kies[21] that strain induced by resin shrinkage during cure is sufficient to cause localized cracking of the resin component in a laminate. If such a phenomenon were to occur on a microscale in a filament-wound structure, there could be associated with it a periodicity in the spacing of the cracks. This effect would be especially noticeable if ideal fiber packing were realized and would furnish a means whereby moisture could cross from one monofilament layer to the next. To explore this possibility, typical epoxy-resin systems were cured in 0.1-mm ID thick-wall Pyrex capillary tubes. The resin mixture was thoroughly degassed in vacuum at 70 C before insertion into the tubes. Granted, Pyrex and E-glass are not quite the same; however, due to the unavailability of E-glass capillary tubing, Pyrex was used. Four groups of ten ten tubes each were prepared. They were:

(1) Untreated glass

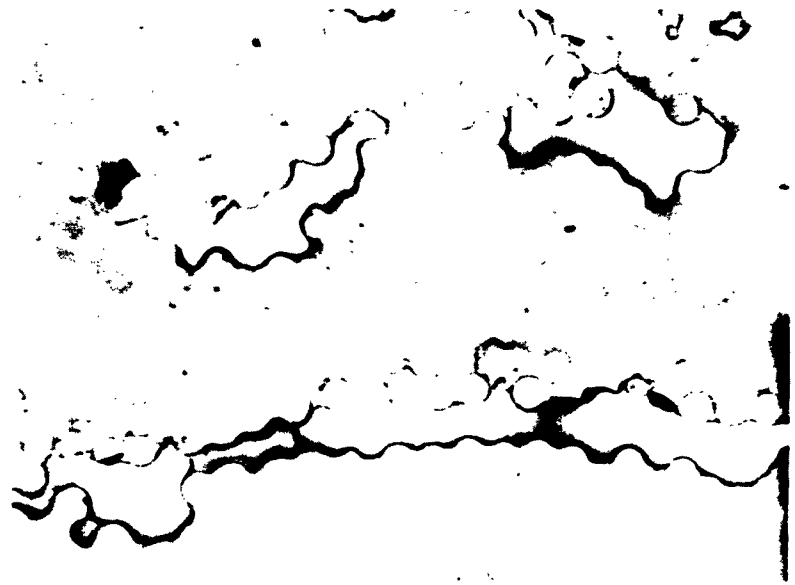
(2) HF etched glass

(3) HF etched glass treated with 1 per cent aqueous A-1100 Silane (γ-aminopropyltriethoxy silane)

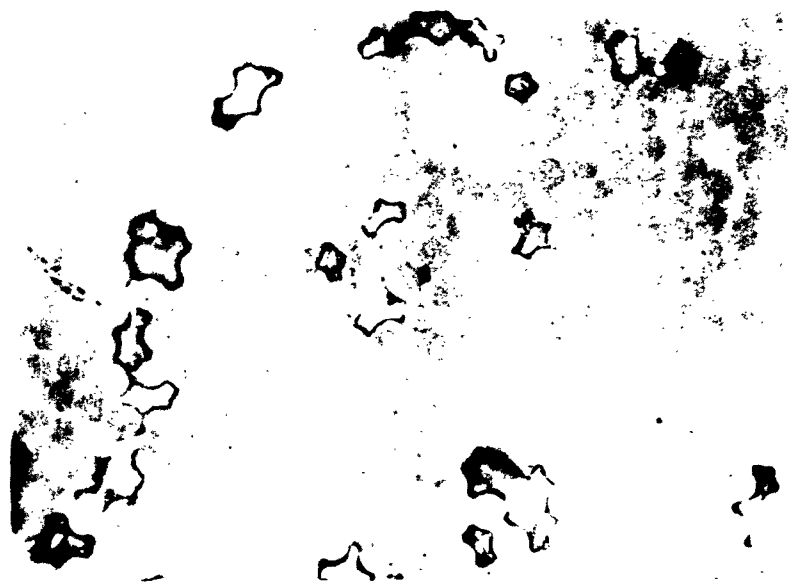
(4) HF etched glass, A-1100 incorporated in resin.

The ends of the capillary were plugged after filling and the contents examined for the presence of air bubbles. They were then placed in a vertical position in a circulating oven, thermostatically controlled at 70 C, and allowed to gel overnight. Five tubes from each group were removed and the remainder postcured as specified in Ser- 634403-691.

100X a.



500X b.



500X c.

FIGURE 6. TYPICAL FIELD FROM WALL CROSS SECTION OF FILAMENT-WOUND CYLINDER

In every instance a few cracks were observed in the resin spaced at random intervals. Unexpectedly, there were almost precisely arranged voids where the resin had pulled away from the wall of the tubing. These were very uniformly spaced (21 per inch) and occurred in all groups except No. 4. The typical appearance of these voids is shown in Figure 7. Figure 8 shows a cross section through the capillary at the level of one of the voids. In Group 4, the resin had separated from the glass uniformly for a considerable distance (as much as 4 inches - Figure 9).

These experiments were repeated using thin-wall capillary tubing (1.5-mm ID, 0.2-mm wall) with the result that the resin "filament" remained intact and void free; however, specific strain patterns were visible upon gelation and upon postcure the glass was observed to shatter in every instance where the resin column was greater than 7/16 inch (32 out of 40 samples). A typical strain pattern is revealed by cross polarizers in Figure 10, and typical glass breaks are shown in Figure 11.

In each instance, the dimensional ratio of filament to supporting medium is considerably different than one would expect to find in a typical filament-wound structure. The only assumptions which should be made are that such phenomena as periodic cracking of one phase is possible. These phenomena will be investigated in systems more closely approximating the structural dimensions of filament-wound composites.

FUTURE WORK

Currently, this program is on schedule. Work has been proceeding simultaneously along two lines: (1) the study of diffusion rates in crosslinked epoxy-resin systems and (2) the study of moisture penetration in filament-wound structures by means of exposure experiments and light microscopy.

During the coming quarter, diffusion effects will be investigated more thoroughly using the equipment constructed for this purpose. In order to compress the time coordinate and evaluate pressure effects upon diffusion rates, a model system (crosslinked gelatin) will be utilized. These data will then be applied to the much slower analogue in crosslinked epoxide resins. Immersion studies will also be continued.

REFERENCES

(1) Fick, A., Ann. Physik, 94, 59 (1855).

(2) Boltzmann, L., Ann. Physik, 53, 959 (1894).

(3) Calvet, E., J. Chim. Phy., 43, 84 (1946).

(4) Hartley, G. S., Trans. Faraday Soc., 42B, 6 (1946).

(5) Crank, J., and Henry, M. E., Trans. Faraday Soc., 45, 1119 (1949).

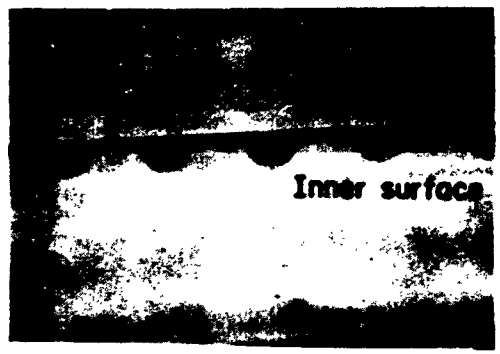


FIGURE 7. PERIODIC VOID FORMATION IN AN EPOXY RESIN CURED IN THICK-WALL PYREX CAPILLARY TUBING

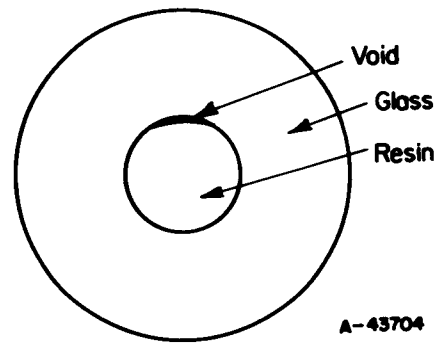


FIGURE 8. CROSS SECTION THROUGH CAPILLARY TUBE AT LEVEL OF TYPICAL VOID

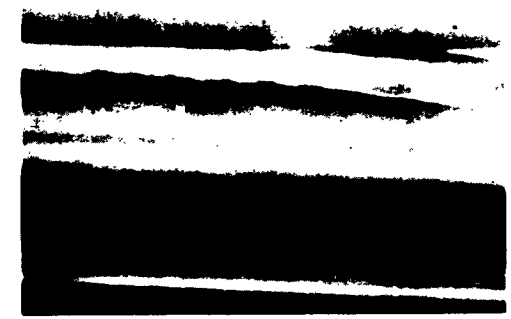


FIGURE 9. UNIFORM SEPARATION OF THE RESIN FROM THE GLASS IN GROUP 4 SAMPLES

FIGURE 10. TYPICAL STRAIN PATTERNS IN THE RESIN GELLED IN THIN-WALL PYREX CAPILLARY TUBING

FIGURE 11. GLASS FRACTURE PRODUCED BY SHRINKAGE DURING POSTCURE

(6) Crank, J., and Henry, M. E., Trans. Faraday Soc., 45, 636 (1949).

(7) Crank, J., Trans. Faraday Soc., 46, 450 (1950).

(8) Stokes, R. H., Trans. Faraday Soc., 48, 887 (1952).

(9) Wagner, C., J. Metals, 4, 91 (1952).

(10) Barrer, R. M., J. Phys. Chem., 61, 178 (1957).

(11) Barrer, R. M., Diffusion in and Through Solids, Cambridge University Press (1951), pp 382-452.

(12) Dean, R. B., Chem. Rev., 41, 503 (1947).

(13) Crank, J., and Park, G. S., Research (London), 4, 515 (1951).

(14) Prager, S., and Long, F. A., J. Am. Chem. Soc., 73, 4072 (1951).

(15) King, G., Trans. Faraday Soc., 41, 325 (1945).

(16) Jost, W., Diffusion in Solids, Liquids, and Gasses. Academic Press Inc., New York, (1952), p 295.

(17) Robinson, C., Proc. Roy. Soc. (London), A204, 339 (1950).

(18) Crank, J., and Robinson, C., Proc. Roy. Soc. (London), A204, 549 (1951).

(19) Ambrose, E. J., J. Sci. Instr., 24, 134.

(20) Encyclopedia of Microscopy, Edited by G. L. Clark, Reinhold Publishing Co. (New York), 1961 (Jonnard), p 505.

(21) Kies, J. A., NRL Report No. 5752 (March 26, 1962).

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APPENDIX

EXPERIMENTAL DATA

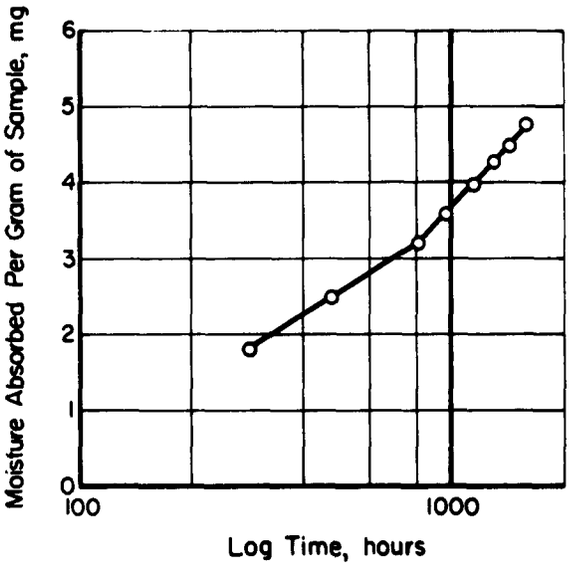

FIGURE A-1. PRESSURE STUDY OF 1-INCH CAPPED RESIN CYLINDERS

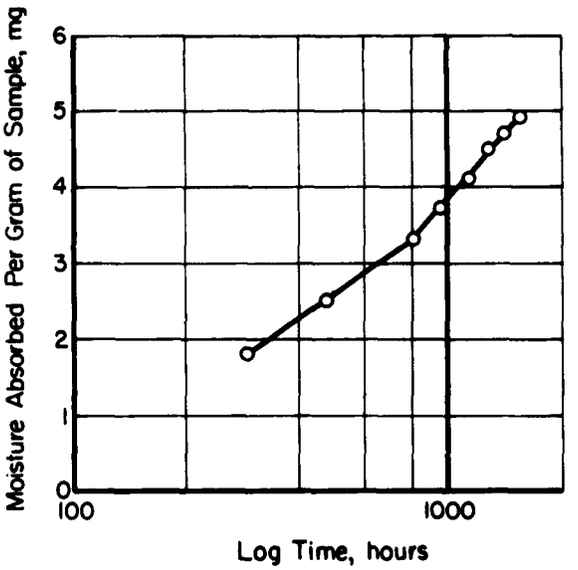

FIGURE A-2. PRESSURE STUDY OF 3/4-INCH CAPPED RESIN CYLINDERS

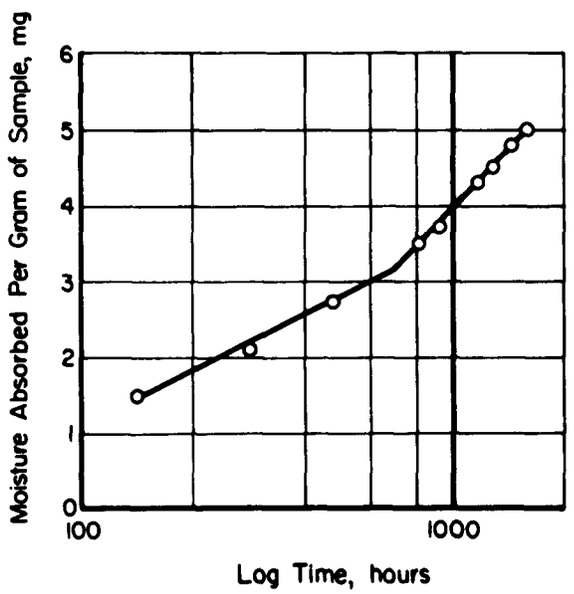

FIGURE A-3. CONTROL EXPERIMENT WITH 1-INCH CAPPED RESIN CYLINDERS

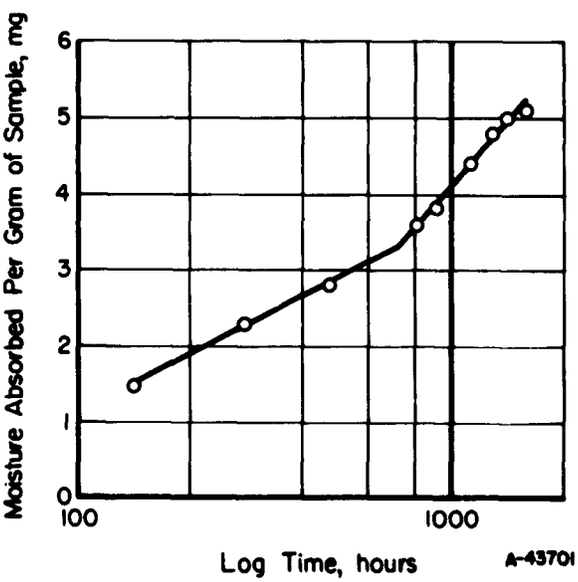

FIGURE A-4. CONTROL EXPERIMENT WITH 3/4-INCH CAPPED RESIN CYLINDERS

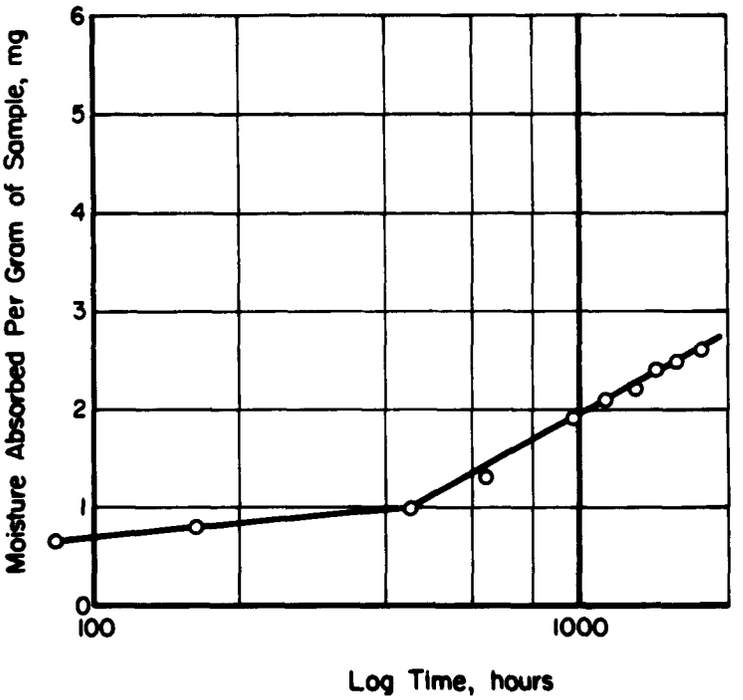

FIGURE A-5. PRESSURE STUDY OF 1-INCH CAPPED FILAMENT-WOUND CYLINDERS

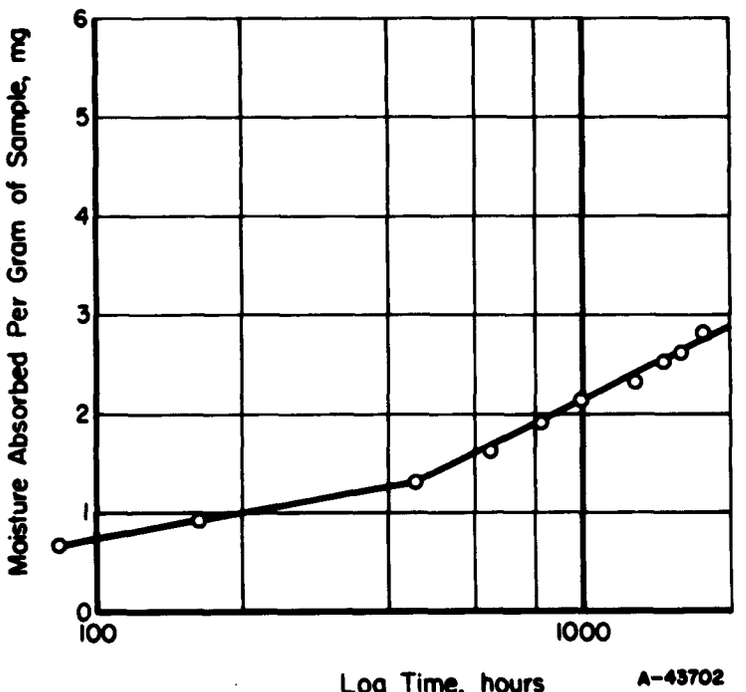

FIGURE A-6. PRESSURE STUDY OF 1/2-INCH CAPPED FILAMENT-WOUND CYLINDERS

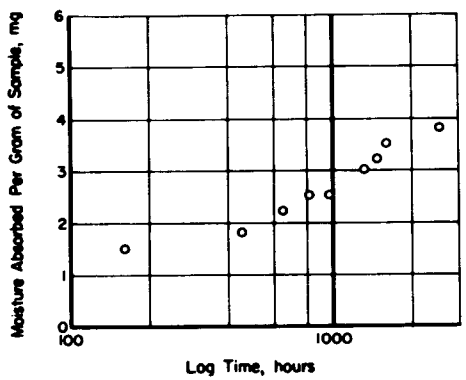

FIGURE A-7. PRESSURE STUDY OF 1-INCH FILAMENT-WOUND OPEN CYLINDERS

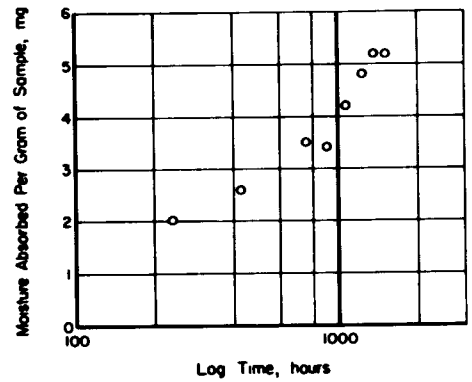

FIGURE A-8. CONTROL EXPERIMENT WITH 1-INCH FILAMENT-WOUND OPEN CYLINDERS

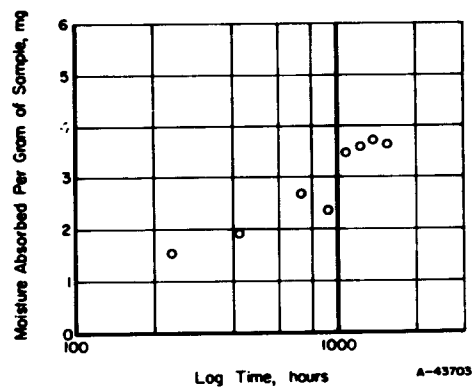

FIGURE A-9. CONTROL EXPERIMENT WITH 1/2-INCH FILAMENT-WOUND OPEN CYLINDERS

TABLE A-1. VOLUMETRIC ANALYSIS OF VOID CONTENT IN TYPICAL FILAMENT-WOUND SAMPLES BY INTEGRATING STAGE METHOD

Traverse Number	Spindle No. 1 (resin/glass)	Spindle No. 2 (Voids)	Total Sample Width, mm
1	4.41	0.51	4.92
2	4.83	0.28	5.11
3	4.74	0.26	5.00
4	5.03	0.47	5.50
5	4.60	0.33	4.93
6	4.69	0.33	5.02
7	4.51	0.50	5.01
8	4.63	0.35	4.98
9	4.60	0.35	4.95
10	4.46	0.47	4.93
Mean	4.65	0.385	5.035

Calculations:

$$\frac{0.385}{5.035} \times 100 = 7.65\% \text{ by volume void content.}$$

Battelle Memorial Institute, Columbus 1, Ohio, MECHANISM OF WATER ABSORPTION IN GLASS-REINFORCED PLASTICS, by D. W. McNeil, B. Bennett, and R. I. Leininger, Second Quarterly Report, January 1, 1963. [22] pp.incl. figures (Proj. SR-007-03-04) (Contract NObs 86871)

Unclassified report

A detailed description of an interferometric method for measuring diffusivity is described. Preliminary data obtained from this device are presented and briefly compared with the results of long-term immersion studies on both cast resin and filament-wound cylinders. Moisture absorption in the former was observed to be a relatively constant phenomenon, while a more random data spread was observed in the filament-wound group.

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